

POLYMER THIN FILMS UNDER SUPERCRITICAL CO₂

In recent years supercritical fluids (SCFs), materials at temperatures and pressures above their critical values, are being used in both traditional industry and new advanced technical areas. The major advantage of SCFs is that their physical properties such as dielectric constant, density, and solubility parameters, can be tuned simply by adjusting the temperature and pressure. Especially, SCFs have also been shown to be effective plasticizers as well as solvents for numerous polymers. In particular, much attention has been focused on CO₂ since it becomes supercritical at a moderate critical temperature and pressure, $T_c = 31.3\text{ }^\circ\text{C}$ at $P_c = 73.8\text{ bar}$, and it is environmentally benign [1].

In spite of its practical importance and numerous studies of the CO₂-induced swelling in bulk polymers, fundamental questions still remain. It is important to understand the interaction of supercritical CO₂ (scCO₂) that can modify diffusion coefficient and the glass transition in thin polymer films. The performance of the many applications of thin films is often dependent on knowledge of the structure and dynamics of the interfaces. Therefore, research in this area will advance understand-

ing of the fundamental physics and applications of polymer thin films.

Neutron reflectivity (NR) is used for quantitative determination of the thicknesses, compositions, and interfacial structures of polymer thin films on a nanometer scale. To achieve this under *in situ* conditions, we have developed a temperature and pressure controlled chamber specifically for neutron reflectivity (Fig. 1). The cell is equipped with two cylindrical sapphire windows. CO₂ is loaded into the cell by means of a manually operated pressure generator. Pressurizing and depressurizing cycles up to 1400 bar are possible. Temperature and pressure stability of the chamber of $\pm 0.1\text{ }^\circ\text{C}$ and $\pm 0.2\%$, respectively can be achieved. Due to the high absorption of neutrons in CO₂, the incident and reflected beams

passed through the Si substrate with a transmission of 0.90 relative to air. It is interesting to note that the background scattering from the CO₂ increases dramatically as the density increases at the phase boundary. Hence the supercritical transition point can be independently monitored with high accuracy.

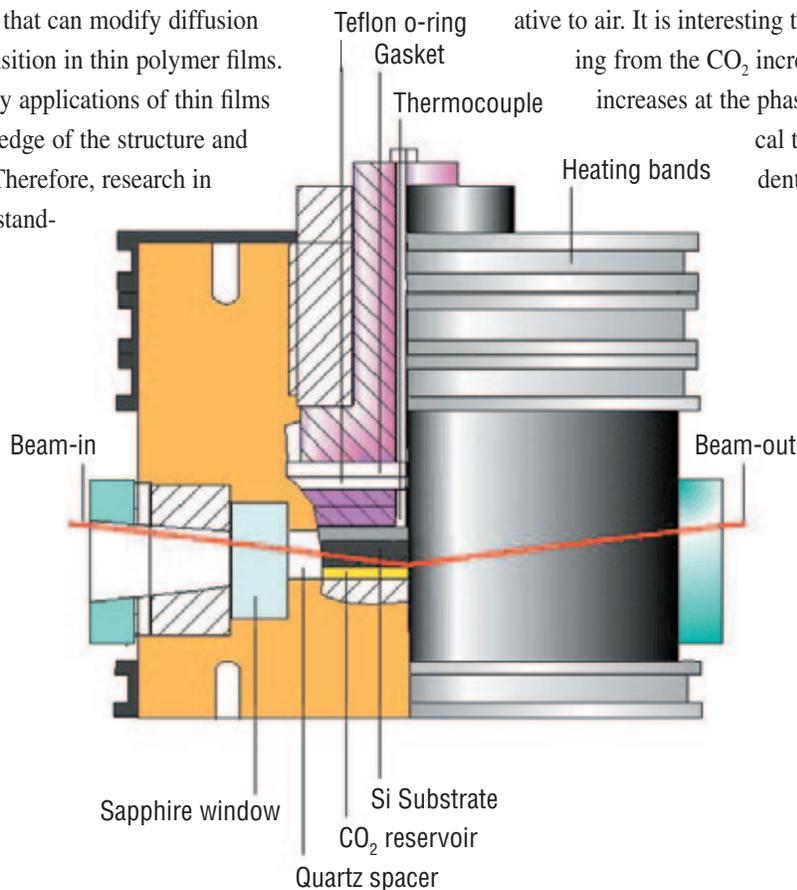


FIGURE 1. Cross-sectional view of the supercritical CO₂ chamber for neutron reflectivity measurements.

In this study we have successfully performed NR measurements of deuterated polystyrene (d-PS) thin films in CO₂ at $P < 700$ bar (Fig. 2). The results show an anomalously large swelling maximum ($\Delta V/V \gg 25\%$) which occurs only at the supercritical fluid/gas phase boundary. Atomic force microscopy confirmed the swelling is uniform throughout the films and does not produce large voids. Such a swelling maximum at the supercritical fluid/gas phase boundary has never been seen in bulk PS-CO₂ mixtures. In addition, an isobaric experiment at 79 bar showed that the same swelling behavior did not appear at the phase boundary between the liquid and supercritical fluid CO₂ phases.

At this point we can only speculate that the anomalous swelling behavior may be related to the higher order nature of the gas/supercritical fluid transition that is accompanied by larger density fluctuations than the first-order liquid/supercritical fluid transition. Experimentally these fluctuations are clearly seen by the sharp increase in background scattering from the CO₂ at the transition boundary. Adsorption of CO₂ into the viscous polymer film may suppress these fluctuations thereby lowering the energy of the sys-

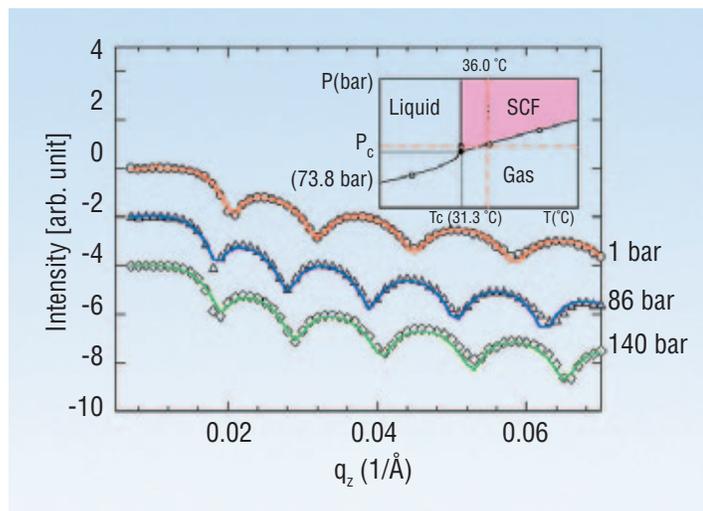


FIGURE 2. Representative reflectivity data for the first pressurization process at $T = 36^\circ\text{C}$. The lines are the best-fit results of the model to the observed density profiles. Swelling is evident in the change of the period of the fringes. Inset: a schematic phase diagram of CO₂ near critical point. The vertical line at 36°C in the inset is the isotherm along which data were taken at pressures of 1, 86, and 140 bar.

tem. This effect was further investigated by observing the swelling of the d-PS film as a function of temperature at $P = 79$ bar (Fig. 3.)

Recently we have expanded our research by measuring chain mobility in bilayer polymer films of d-PS and hydrogenated PS (h-PS). We have used secondary ion mass spectrometry and NR to measure the diffusion coefficient as a function of pressure, temperature and molecular weight. This work established that swelling at the phase boundary is accompanied by an increase in interdiffusion between the polymer layers and a large decrease in the PS glass transition temperature. These results show that scCO₂ can potentially be used to process multi-component thin polymer films that may otherwise not be miscible. Potential applications are in the areas of graded index of refraction waveguides and lower dielectric constant films for use in microelectronic devices.

REFERENCES

- [1] M.A. McHugh and V.J. Krukonic, *Supercritical Fluid Extraction*, 2nd Ed., Butterworth-Heinemann, 1993.

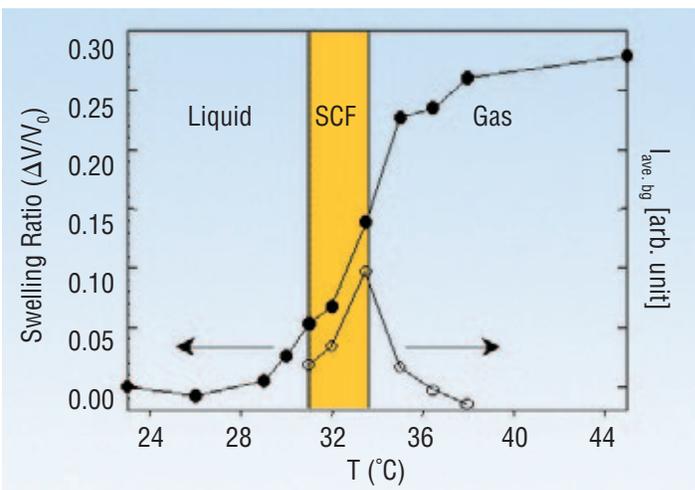


FIGURE 3. Temperature dependence of the swelling of polystyrene at $P = 79$ bar (filled circles). Open circles show the averaged background intensity as a function of temperature.